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A FLUORIMETRIC METHOD FOR THE DETERMINATION OF CYANIDE WITH FLUORESCEIN AND IODINE *

KEY WORDS: Fluorimetric method, cyanide, fluorescein, iodine

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ABSTRACT

A rapid, simple and sensitive fluorimetric method has been developed for the determination of cyanide with fluorescein as fluorogenic reagent ($\lambda_{ex}=494$ nm, $\lambda_{em}=514$ nm) at pH 6.0–7.0. A linear calibration curve was obtained in the range 0.004–2.0 μg CN^- / 25 ml. The detection limit is 0.004 μg CN^- / 25 ml. The method was successfully applied to the determination of cyanide in waste water.

INTRODUCTION

The fluorimetric methods for determination of cyanide have been reviewed and critically studied[1]. Guilbault and Kramer[2] pro-

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posed a specific method for the determination of cyanide using various quinone derivatives. This method is simple, direct and highly selective. Rubio[3] described a kinetic, fluorimetric method for the determination of traces of cyanide with pyridoxal–5– phosphate oxalyldydrazone (PPOH). The method is highly selective and sensitive. The above–mentioned methods are regarded as the best fluorimetric methods for the determination of cyanide. In this work, a new method for the determination of cyanide has been described. Iodine reacts with flourescein to produce a non–fluorescence species. If cyanide is present, the following reaction happens: $I_2+CN^- = ICN+I^-$. Hence, the fluorescence intensity of the solution increases with the increasing concentration of cyanide when appropriate amounts of iodine and fluorescein are added. The phenomenon can be made use of to determine cyanide.

This new method has some advantages, such as simplicity, rapidity, stability and sensitivity, in comparison with other fluorimetric methods.

EXPERIMENTAL

Apparatus

RF–540 spectrofluorimeter (Shimadzu, Kyoto, Japan) was used.

Reagents

All chemicals were of analytical reagent grade.

Cyanide ion standard solutions. A stock solution (1.000 mg / ml) was prepared by dissolving 0.1884 g sodium cyanide (NaCN) in water and diluting to volume in a 100–ml standard flask. The stock solution was diluted to 1.00 μg / ml with water as working solution.

Fluorescein solution (1.0×10^{-4}M). Prepared by dissolving 0.0166 g fluorescein in water and diluting to volume in a 500–ml standard flask.

Iodine solution. A stock solution (1.000 mg / ml) was prepared by dissolving 0.1000 g iodine in 100% ethanol and diluting to volume in a 100–ml standard flask. The solution was diluted to 20 μg / ml with 100% ethanol as working solution. Iodine solution (20μg / ml) must be prepared before use.

Buffer solution (pH 6.4): Mix 2 volume of 1 / 30 M KH_2PO_4 with 1 volume of 1 / 30 M Na_2HPO_4.

Procedure

Take appropriate amounts of cyanide standard solution into a 25.00 ml volumetric flask, add 1.50 ml of buffer solution, 1.60 ml of 20μg / ml iodine solution and 1.0 ml of 1.0×10^{-4}M fluorescein solution, dilute to the mark, mix. Measure the fluorescence intensity at 514 nm (with excitation at 494 nm) against a reagent blank within 10 hours.

RESULTS AND DISCUSSION

Spectral characteristics

As shown in Fig. 1, the excitation and the emission spectra of the fluorescein $-I_2$ and fluorescein– I_2–CN^- system are similar to each other. The excitation and emission are at 494 and 514 nm, respectively. However, the fluorescence intensity of fluorescein–I_2 system increases when CN^- is added.

The optimum conditions for fluorimetric determination

The experimental results indicated that the maximum fluorescence intensity was achieved when 1.00 ml of 1.0×10^{-4}M

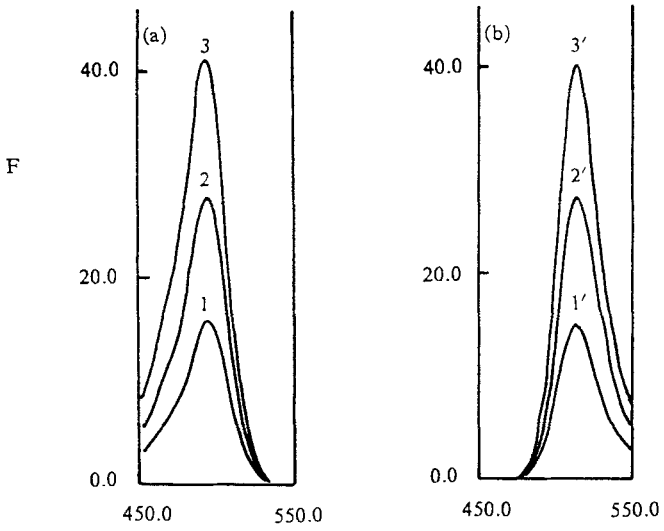

Fig.1, Excitation (a) and emission (b) spectra of the fluorescein–I_2 system (1,1′) and fluorescein –I_2–CN^- system : 1μg CN^- / 25ml(2,2′), 2μg CN^- / 25 ml(3,3′)

fluorescein solution and 1.60 ml of 20 μg / ml iodine solution were employed.

The maximum fluorescence intensity occurs over the pH range 6.0–7.0. A pH of 6.4 is recommended for use, achieved via addition of 1.5 ml of buffer solution per 25 ml of final solution.

The influence of setting time was investigated. The results indicated that the reaction was finished immediately and the difference in fluorescence intensity between the fluorescein–I_2– CN^- and fluorescein–I_2 blank remain constant within 10 hours.

Effect of foreign ions

The tolerance limits of some ions for the determination of 1.0 μg CN^- by the described procedure were studied. When the ralative error is less than $\pm$ 5%, the following ions have no effect: nitrate, citrate, chlorate, perchlorate, chloride, iodide, iodate, bromide, fluoride, sulfate, tartrate, phosphite, phosphate, phthalate, bicarbonate, molybdate, carbonate, borate, perborate, tungstate, silicate, bromate, ferricyanide, dichromate. However, up to 10–fold of $S_2O_3^{2-}$, 3–fold of SO_3^{2-}, 2–fold of As^{3+} and 0.5–fold of SCN^- interfere in the determination. The interferences of these ions can be eliminated by the following distillation procedure.

Separation of cyanide by distillation

Place the sample containing cyanide in a 500–ml all–glass distillation apparatus. Add 0.5 ml of 30% perhydroxide, 1 mg of zinc ion and 2 mg of baric ion. Then adjust pH value of the solution to 7 by dropping 0.1 M HCl, add extra 0.5 ml of 0.1 M HCl, and dilute to 50 ml with distilled water. Connect up the distillation apparatus, distill rapidly, collect the distillate in a volumetric flask containing 10 ml of 0.1 M sodium hydroxide. Stop distilling when distillate volume reaches 40 ml, adjust pH value to 6.4 with 0.2 M HCl and add 2 ml of buffer solution, and then dilute it to volume in a 50–ml standard flask with distilled water. Determine cyanide in an aliquot according to the procedure given in Experimental.

Calibration graph

The calibration graph for the determination of CN^- was constructed under the optimum conditions. Good linearity of CN^- concentration was observed in the 0.004–2.0 μg / 25 ml range. The regression equation and correlation coefficient fit by the least square

Table 1 Analysis of synthetic mixtures

Sample	Composition of mixtures*	Recovery of CN^-** (%)
A	NaCl (1.0g)+Na_2SO_3(2.0 mg) $MgCl_2$(1.0g)+NaCN(20μg)	99
B	KSCN (20 mg)+As_2O_3 (20 mg) NaCl (1.0g) +NaCN (20μg)	102

* The mixtures should be analysed after distillation, and adjusted pH value to 7 by dropping HCl or NaOH.

** Average of three determinations

Table 2 Analysis of wate water*

Sample	Found of CN^- (μg / ml)**		Added (μg / ml)	Found (μg / ml)
	Rubio's method	This method		
A	1.6	1.5	2.0	2.0
B	7.3	7.5	2.0	1.9

* From an electroplating Works

** Average of six determinations

method are: $\triangle F = 23.1\ C - 0.5$, $r = 0.9998$ (the unit of C is $\mu g\ CN^-$ / 25 ml).

Application

This method has been successfully applied to determine CN^- in two synthetic mixtures (Table 1) and waste water (Table 2). The possibility of using this method for analysis of the samples was tested by determining the recovery of known amounts of CN^- added to the sample. The results in table 1 and 2 show that the recoveries of CN^- for the synthetic mixtures and samples tested are 98–102%. The reproducibility of the determinations was good. In addition, the CN^- content in waste water was determined by two methods: the proposed method and Rubio's method. The results obtained are shown in Table 2. It can be observed that both series of values are in good agreement.

CONCLUSION

The proposed method is a high sensitivity and selectivity fluorimetric method for determination of cyanide ion. The procedure is rapid, simple and the results are reproducible.

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